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Electrospinning and optical properties of polyacrylonitrile / carbon quantum dots fluorescent nanocomposite nanofibres

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The optical properties and structural characteristics of polyacrylonitrile nanofibres containing two different types of fluorescent compounds, prepared by an electrospinning technique have been studied. The electrospinning solution has been prepared by dissolving the PAN powder at various concentrations in N,N- dimethyl formamide. Carbon quantum dots nanoparticles (CQD) as a fluorescent agent, and Disperse Blue 354 as a fluorescent dye, have been used to produce fluorescent composite nanofibres. The effect of the fluorescent agent on the optical properties of the nanofibres has been evaluated by producing nanofibres with fluorescent dye or CQD nanoparticles at various concentrations. The structural and optical properties of the collected composites nanofibres are characterized using polarizing optical microscopy, field emission-scanning electron microscopy and photoluminescence spectrometry. The results show that the emission and fluorescent properties of the nanofibres depend on the nanofibres diameter, and the type and concentration of the fluorescent materials. The fluorescence intensity is increased with decreasing diameter of the fluorescent nanofibres. In addition, the emission of the nanofibres containing the CQDs is greater than that of the pure nanofibres and nanofibres with the fluorescent dye.

Keywords*:* Electrospinning, Fluorescent fibre, Optical properties, Nanofibres, Nanocomposite, Polyacrylonitrile

1 Introduction

Recently, nanocomposites have attracted great interest due to their unique applications in many fields, including biosensors, optical devices, sensing materials, biomedical science and energy storage[1,2]. There are various processing techniques for producing nanocomposite; among these methods electrospinning is a simple, straightforward, unique, efficient and cost-effective technique for fabrication of nanocomposites, with the fibres ranging from microns to a few nanometers in diameter[3]. Nanofibres produced by this technique have several remarkable advantages, including high surface area-to-volume ratio and small diameter. As a result, this technique has various applications in, for instance, biomedical fields such as drug delivery systems and tissue engineering, nanocatalysis, filtration, fuel cell membranes, sensing materials and optical electronics[3-5]. Both natural and synthetic polymers have been used to produce nano-scale fibres. By using the electrospinning technique, various nanofibres with fluorescent properties have been prepared, such as nanoparticle-polyelectrolyte ultra-fine fibres[6], quantum dot – poly vinyl alcohol composite nanofibres, and polyvinylpyrrolidone/ dye nanofibres[8]. Several researchers have fabricated pure and composite (poly acrylonitrile) (PAN) nanofibers by an electrospinning method[9-11]. For example, Sichani *et al*.[9] fabricated PAN nanofibres with Ag nano particles to investigate their antibacterial properties and as uniaxially aligned fibers[10] by electrospinning techniques. Another study focused on the effect of the electrospinning parameters on PAN nanofibre diameter[11].

Combining dye molecules and/or nanoparticles with polymers in electrospinning can improve the nanofibres properties, such as optical properties, etc. For example, polyvinyl alcohol/ CdSe-ZnS (CdSe-ZnS core-shell quantum dots) composite nanofibres showed a unique fluorescent phenomenon[12]. Semi-conductor quantum dots are very small, colloidal nanocrystals that have been widely used because of their broad range of desirable and unique optoelectronic and optical properties, including negligible photobleaching, narrow emission spectra, high photochemical stability and broad excitation spectra[13,14]. They have been used in various applications, such as light emitting diodes, biological

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labeling, solar cells, biotechnology, lasers, optoelectronic devices, sensors and biosensors[15,16]. There are also various types of dopants, such as special dyes, which can produce nanofibres with special optical properties[7]. Polymers that are doped with dyes can change light radiations over a broad range of spectra and with change in dye or polymer structure, these properties can be controlled. Dye-doped nanofibres have been described as potential candidates for use as nanometric light sources, photoconverters and optical waveguides[7,17,18].

As mentioned above, modifying the optical properties of fluorescent nanofibres is a very interesting subject. Up to now, several researchers have studied the morphology and optical properties of electrospun nanofibres but to the best of my knowledge only a few studies have been reported about the optical properties of nanofibres of polymers combined with a fluorescent dye as CQDs. The objective of the work described here is to enhance and evaluate the optical properties of nanocomposites of fluorescent dye/PAN and CQDs/PAN nanofibres. For this, pure PAN nanofibres and PAN nanofibres containing various amounts of fluorescent material (CQDs or fluorescent dye) have been successfully prepared by an electrospinning technique. The effects of the fluorescent compounds and the electrospun nanofibre morphology on the optical properties of the developed nanocomposite nanofibres are investigated.

2 Materials and Methods

Polyacrylonitrile (PAN), with weight average molecular weight (M_w) of 70000 g/mol, was purchased from Isfahan Polyacrylic Co., Iran. N'N-dimethyl formamide (M= 73.10 g/mol) was obtained from Merck Co., Germany and used as a solvent. A fluorescent dye (C.I. Disperse Blue 354, $C_{31}H_{37}N_3O_2S$) with 515.70 g/mol molecular weight was supplied by Yekrang Co., Iran. Carbon quantum dots (CQDs) nanoparticles, with 2 nm diameter, were supplied by Sari Tejarat Co., Iran.

A polarized light optical microscope (Nikon Microphot-FXA, Nikon Co., Japan) was used for the study of the nanofibres shape. The morphology and diameters of the nanofibres were characterized using scanning electron microscopy (SEM; Hitachi model S-4160, Japan- Daypetronic company). The optical properties of the nanofibres nanocomposites were examined at room temperature using an optical fluorescence spectrophotometer (LS-55, Perkin Elmer, UK).

The electrospinning setup, consisted of a positive electrode connected to a syringe pump (STC-523, Terumo, Japan), a spinneret that was connected to a high voltage supply (Gamma High Voltage Research Inc. USA) (between 0 and 25 kV) and a negative electrode connected to a flat plate, aluminum collector, was used.

2.1 Preparation of Electrospinning Solutions

In the first step, the electrospinning solution was prepared by dissolving the PAN at 10, 12, 15, 18 and 20 wt% solution concentrations in DMF by continuous agitation in a stirrer for 3 h at ambient temperature (25±2^{o}C). Then, Disperse Blue 354 (fluorescent dye) at 0.04, 0.08, 0.8, 4.0 and 8.5 wt% solution concentrations, or CQDs nanoparticles (fluorescent agent) at 0.005, 0.01 and 0.02 wt% solution concentrations, both relative to the PAN content, were added into the PAN solutions and stirred thoroughly for 24h at room temperature (25±2 ^{o}C) to produce solutions for electrospinning of the fluorescent composite nanofibres. The resulting PAN/fluorescent dye or PAN/CQDs solutions with various CQDs and fluorescent dye loadings were kept in closed cap vessels at ambient temperature (25±2 ^{o}C). for 24h before electrospinning.

2.2 Electrospinning of Nanofibres Nanocomposite

The prepared electrospinning solutions were injected into a 5 mL syringe (outer diameter of the syringe needle 0.6 mm). To generate spinning jets, a high-voltage DC power supply in the range of 0-25 kV was used. The cathode of the high-voltage DC supply was connected to the syringe needle and the grounding electrode was attached to an aluminum plate (as a flat collector) for accumulating the electrospun nanofibres. All the electrospinnings were carried out at room temperature (25±2 ^{o}C); the pure PAN nanofibres and fluorescent PAN nanofibres were separately prepared in three ranges of diameters.

3 Results and Discussion

In order to produce pure PAN nanofibres with significant diameter differences, we have investigated the effect of PAN solution concentration on the fibre formation. To obtain the optimal polymer concentration, solutions with various concentrations (10, 12, 15, 18 and 20 w/w %) are prepared with the spinning conditions, such as 5-14 kV applied voltage, 10,12 and 15 cm niddle-to-collector distance, and 0.01, 0.1, 0.2, 0.3, 0.5, 1, 1.5 and 2 mL/h injection rate. According to optical microscope images of the

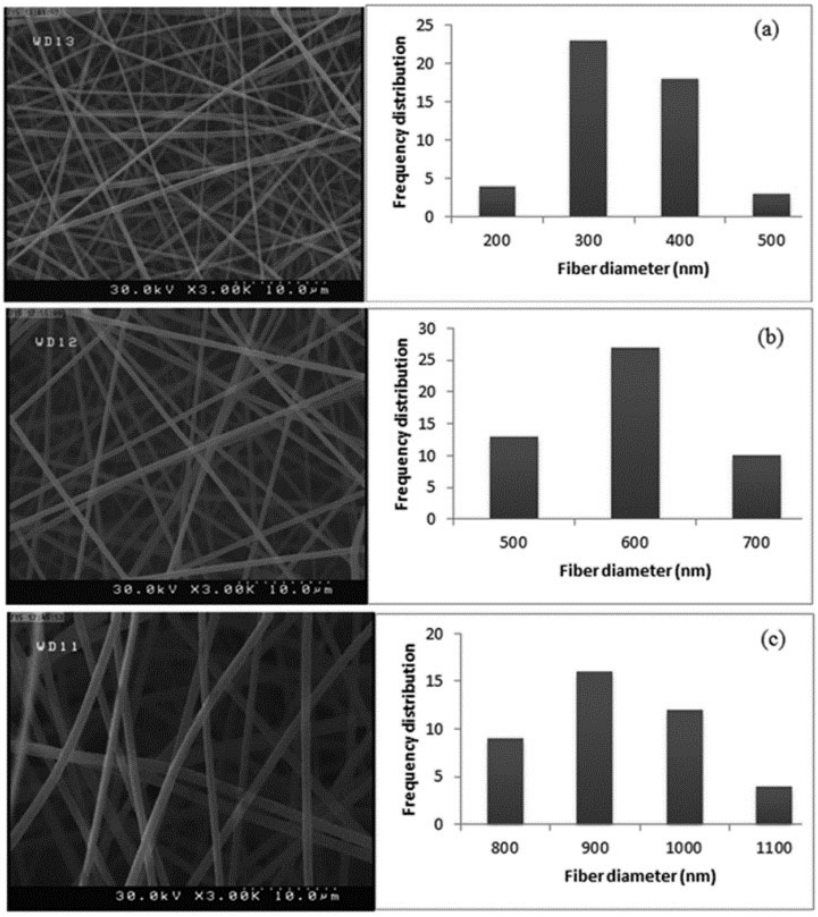

Fig. 1 — SEM images and diameter distributions of pure PAN nanofibres at (a) 12%, (b) 15% and (c) 18 wt % concentrations (magnification ×10µm)

PAN nanofibres electrospun at the various concentrations the nanofibres containing 10% PAN polymer show a non-uniform morphology with many beads. By increasing the concentration of the PAN polymer, the uniformity of the nanofibres is increased and nanofibres without beads are formed. Indeed, in the electrospinning technique, at a critical concentration of polymer solution (12 wt%), entanglements of the polymer chains overcomes the solution surface tension and beads-free nanofibres are formed. In the electrospinning of the PAN nanofibres, at the highest concentration of polymer solution used (20 wt%), due to an excessive increase in the solution viscosity, an un-stretchable droplet in the applied field is formed, and electrospinning of nanofibres does not become possible. Therefore, electrospun nanofibres obtained at 12, 15 and 18 wt% PAN solution concentrations that shows bead free, smooth and uniform morphology, are chosen for further studies.

After determining the optimum concentration of the PAN solutions, the effect of various parameters on the electrospinning, such as applied voltage, collection distance and injection rate, has been investigated. In the used conditions for electrospinning of nanofibres with the three concentrations of pure polymer and those containing dyes or CQDs, the applied voltage is kept 10 kV, the needle-to-collector distance is 15 cm and the injection rate is 0.3 mL/h. In order to fabricate fluorescent composite nanofibres, various concentrations of CQDs (0.005, 0.01 and 0.02 wt%, relative to the PAN content) dissolved in 15% PAN solution are used. In addition, to prepare fluorescent dye/PAN composite nanofibres, various concentrations of disperse dye (0.04, 0.08, 0.8, 4 and 8.5 wt%) are added to 12, 15 and 18 % PAN solutions and electrospinning is done.

3.1 Morphology and Diameter of PAN Nanofibres

The morphologies of the nanofibres are evaluated by SEM. The images of the pure PAN nanofibres spun from the three concentrations (12, 15 and 18 wt%), are shown in Fig. 1. The PAN nanofibres has smooth surfaces and bead free morphologies. For producing

diameter distribution graphs, the diameters of the PAN nanofibres are measured by Image J software. The diameter distributions of the nanofibres for the concentrations of 12, 15 and 18% PAN are also shown in Figs 1(a), (b) and (c) respectively. The diameters and standard deviations of the produced PAN nanofibres are 280 ± 8.91, 562 ± 10.90 and 870 ± 18.82 nm respectively. According to Fig. 1, the diameter of the electrospun nanofibres increases, as expected, with increasing concentration of the PAN. When the concentration of PAN is increased, a larger amount of entangled polymer chains exit in a constant volume of the solution. As a result, by increasing the polymer concentration, the PAN nanofibre diameter increases. Similar results have been reported by Morshed *et al*.[9].

3.2 Effect of Fluorescent Compounds Concentration on PAN Nanofibres Diameter

SEM images of the PAN (15wt%) nanofibres with various concentrations of CQDs (0.005, 0.01 and 0.02wt%) are shown in Fig. 2. The CQDs change the characteristics of the electrospinning solution, and the electrospun PAN nanofibres diameters increase significantly with adding CQDs to the PAN solution, while with increasing concentration of the CQDs the nanofibres diameters increase under the same electrospinning conditions. The conductivity and viscosity of the electrospinning solutions are the most important parameters in the electrospinning technique. By increasing the concentration of CQDs in the solution, the viscosity of the electrospinning solution changes therefore the diameter of nanofibres is increased. On the other hand, as reported earlier[19], by increasing the conductivity of solution the fibres diameter decrease. By adding CQDs to the PAN solution, the charge density decreases; therefore, a weaker elongation force is applied on the ejected jet for the same applied voltage. This phenomenon leads to the formation of nanofibres with larger diameters, as shown in the diameter histograms (Fig. 2).

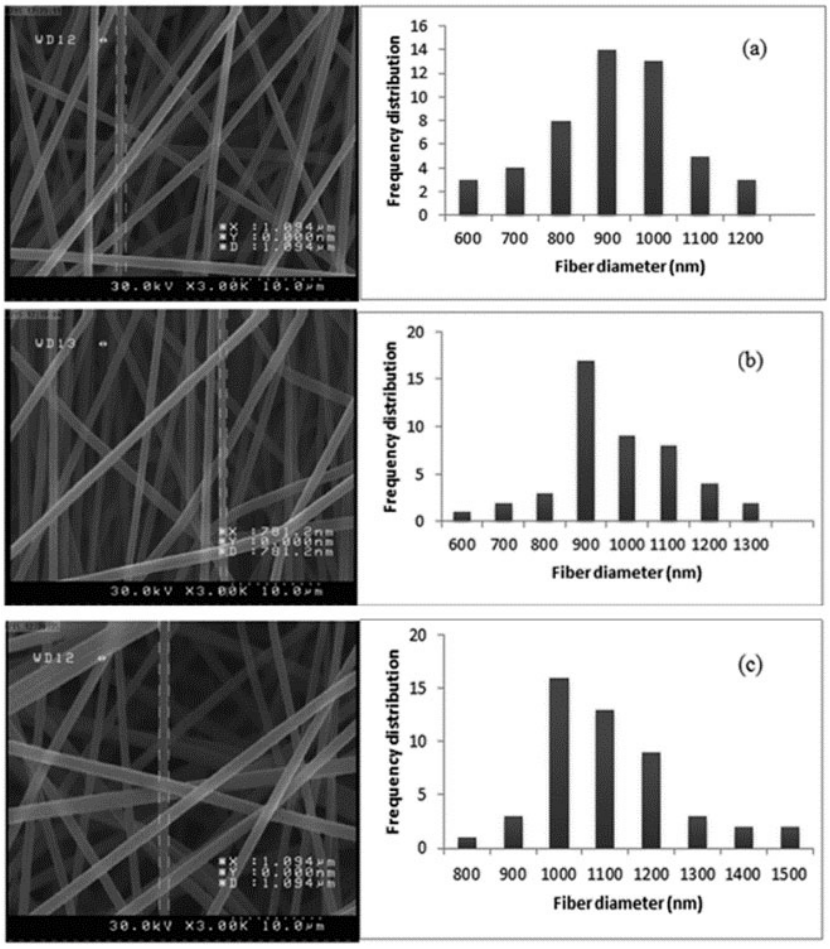

Fig. 2 — SEM images and diameter distribution of PAN/CQDs nanofibres composite with constant concentrations of PAN (15 wt%) and various concentrations of CQDs (a) 0.005, (b) 0.01 and (c) 0.02wt% (magnification ×10μm)

The diameter distributions of the nanofibres composite for the concentration of 15% PAN polymer and CQDs (0.005, 0.01 and 0.02%wt) are also shown in Figs 2 (a), (b) and (c). The average diameters and standard deviations of the resulting PAN/CQDs nanofibres are 905 ± 19.41, 958 ± 19.02 and 992 ± 19.22 nm respectively.

The SEM images of the PAN/fluorescent dye composite nanofibres (with fluorescent dye concentrations of 0.04%, 0.08%, 0.8%, 4% and 8.5 wt% and 15wt% PAN) are shown in Fig. 3. As shown in this figure, with increasing dye concentration no significant change in the fibers diameter is observed, except at 8.5% concentration of dye, for which there was a considerable increase in nanofibres diameter. The diameter distributions of the composite nanofibres with 15% PAN concentration and dye concentrations of 0.04, 0.08, 0.8, 4 and 8.5 wt% are also shown in Figs 3 (a-e). The average diameters and standard deviations of the resulting PAN/dye nanofibres are 570 ± 12.28, 599 ± 13.07, 550 ± 11.69, 564 ± 10.10 and 1210 ± 21.79 nm, respectively, while the average diameter of the pure PAN nanofibre is 562 nm [Fig. 1 (b)]. Therefore, by increasing the dye concentration up to 4% wt, the diameter change is not significant, but the diameter is significantly increased with increasing the dye concentration from 4% to 8.5%.

3.3 Effect of Fluorescent Dye and CQDs Concentration on Photoluminescence Properties of Nanofibres Composite

The effect of nanofibres diameter and dye/CQDs concentration on the optical properties of the nanofibres, including their fluorescence intensity are charactrized using optical fluorescence spectrophotometer. The fluorescence spectra of the PAN/fluorescent dye and PAN/CQDs composite nanofibres with 15% concentration of PAN polymer and various fluorescent dye and CQDs loadings are shown in Figs 4 (a) and (b). All fluorescence spectra are measured with an excitation light of 338 nm wave length. According to Fig. 4(a), at a concentration of 0.04 wt% fluorescent dye, the PL intensity of the nanofibres does not change with addition dye, The PL intensity of the nanofibres first increase significantly for 0.08% dye with maximum emission occuring at about 404 nm; then, due to a fluorescence quenching phenomenon, the PL intensity decreased. As shown in Fig. 4(a), with increasing the CQDs concentrations the PL intensity of the nanofibres first does not change (up to 0.01 wt %) and then increases significantly when the CQDs concentration is

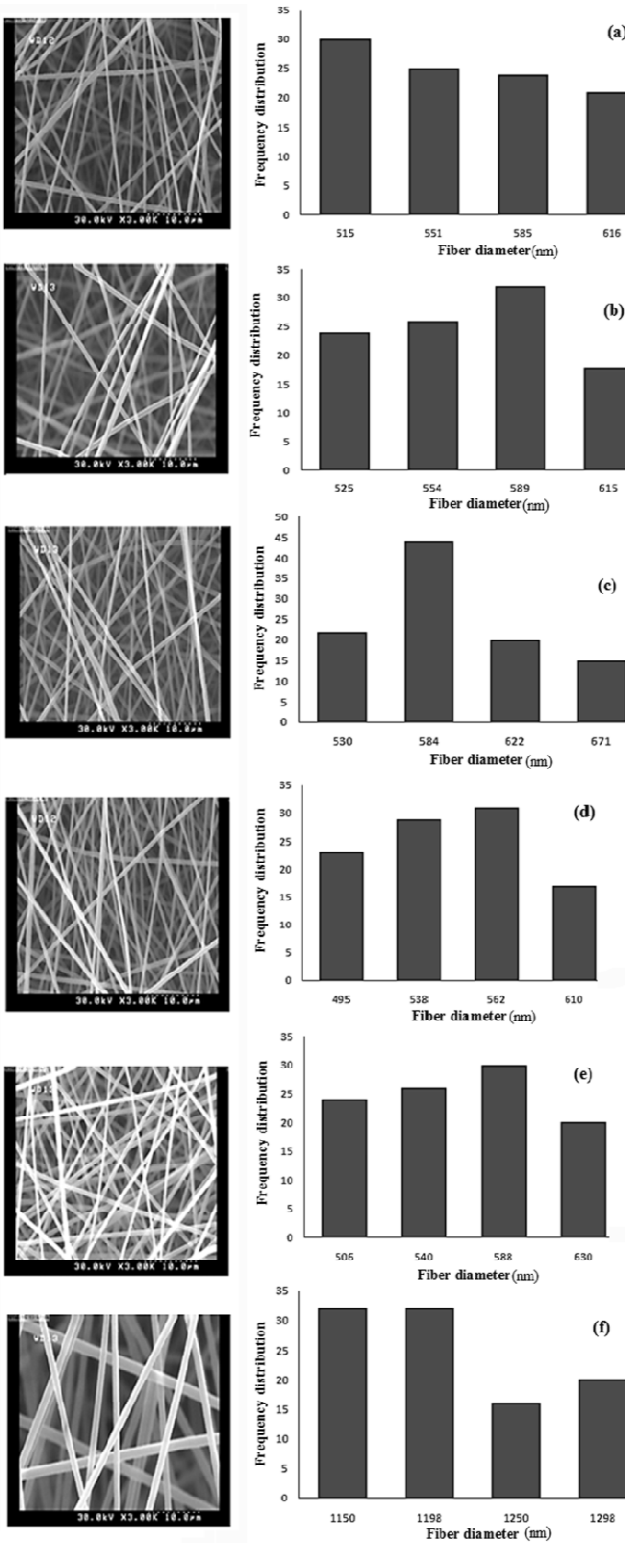

Fig. 3 — SEM images and diameter distribution of PAN/fluorescent dye composite nanofibres with constant concentrations of PAN (15 wt%) and (a) 0%, (b) 0.04%, (c) 0.08%, (d) 0.8%, (e) 4% and (f) 8.5Wt % concentration of fluorescent dye

0.02%; the PL intensity is also found maximum at about 402 nm.

The fluorescence spectra of pure PAN and the PAN/fluorescent dye and PAN/CQDs nanofibres with maximum PL intensities are shown in Fig. 4 (c). It can be seen that the photoluminescence intensity of the PAN/fluorescent dye is much less than that of the PAN/CQDs nanofibres even though four times as much dye is added. The quantum dots nanoparticles have sharper and narrower emission spectrum of fluorescent dye. This is probably due to the size of the quantum dots and the better dispersion of these nanoparticles. These results are in agreement with the earlier findings[20]. This figure clearly demonstrates that the CQDs has more PL intensity than the fluorescent dye due to its high fluorescence quantum yield.

According to the fluorescent emission of the nanofibres containing fluorescent dye, the optimum concentration of fluorescent dye is achieved at 0.08 Wt% for the 15wt% PAN solution. Therefore, fibres with this same dye/polymer ratio are prepared for PAN with concentrations of 12wt% and 18wt% and the variations in fibre diameters of these samples are examined. SEM images of the PAN/ fluorescent dye fibres of these samples are shown in Fig 5. The diameter distribution of the nanofibres composite for concentrations of 12 and 18 wt% PAN polymer and fluorescent dye (0.078 and 0.081% respectively) are shown in Figs 6 (a) and (b). The average diameters

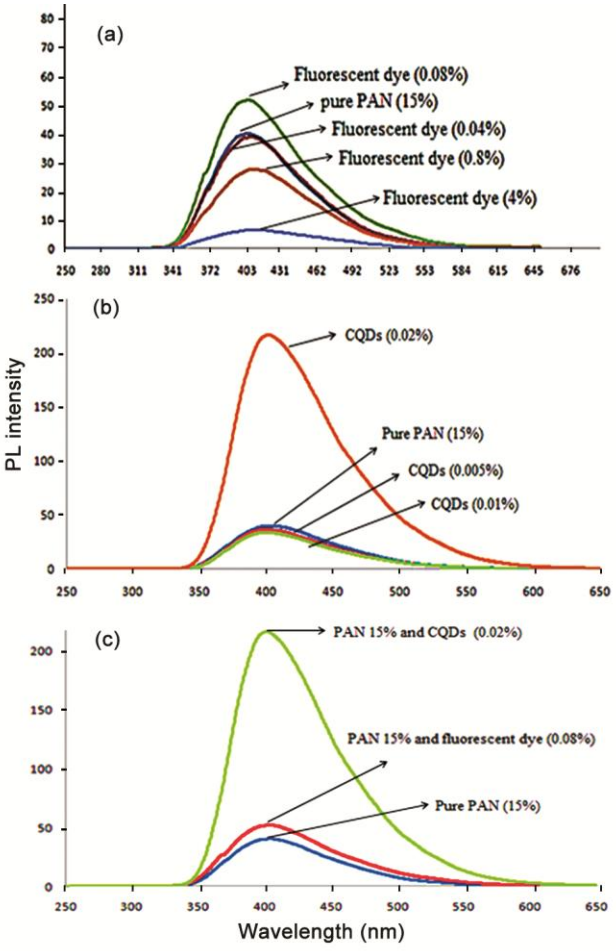

Fig. 4 — Fluorescence spectra of the pure PAN and (a) PAN/fluorescent dye, (b) PAN/ CQDs nanofibers composite with various fluorescent dye and CQDs loadings and (c) PAN/CQDs and PAN/ fluorescent dye

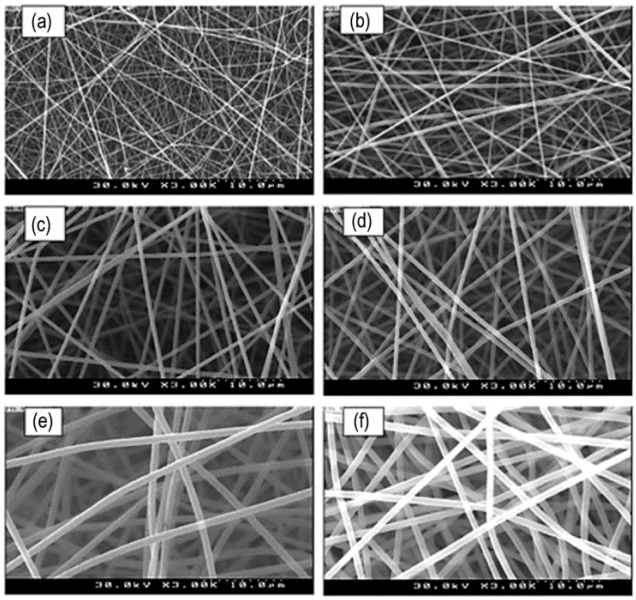

Fig. 5 — SEM images of nanofibres with (a) pure PAN 12 wt%, (b) PAN 12 wt% and fluorescent dye 0.078 wt%, (c) pure PAN 15 wt%, (d) PAN 15 wt% and fluorescent dye 0.080 wt%, (e) pure PAN 18 wt% and (f) PAN 18 wt% and fluorescent dye 0.081 wt% (magnification ×10μm)

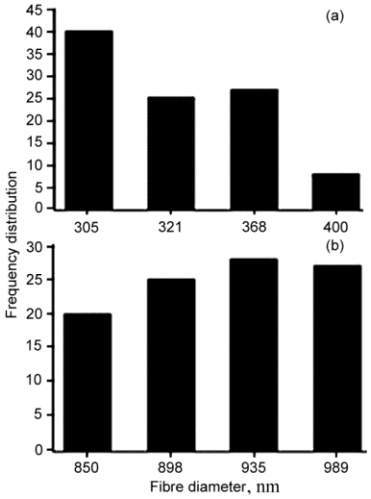

Fig. 6 — Diameter distributions of the PAN/dye nanofibres composite (a) 12 wt% PAN polymer and 0.078 wt% fluorescent dye, and (b) 18 wt% PAN polymer and 0.081 wt% fluorescent dye

Table 1 — Diameter of pure PAN and PAN/dye composite nanofibres

Concentration of PAN polymer %wt	Concentration of fluorescent dye % wt	Nanofibres diameter nm
12	0	280 ± 8.91
12	0.078	335± 12.08
15	0	562 ± 10.90
15	0.080	599± 13.07
18	0	870 ± 18.82
18	0.081	920± 17.83

and standard deviations of the resulting PAN/dye nanofibres are 335±12.08 and 920±17.83 respectively. Table 1 shows the diameters of the pure PAN (with various concentrations) and PAN/dye composite nanofibres. It is observed that the diameter differences between the pure PAN nanofibres and PAN/dye composite nanofibres are almost the same for all three concentrations (12, 15 and 18 wt%), but the per cent of the diameter differs greatly.

4 Conclusion

This study describes the effect of fluorescent materials on the optical properties of electrospun PAN nanofibres. The pure PAN nanofibres and PAN nanofibres containing fluorescent compounds are produced by an electrospinning method. The effects of the fluorescent agents and nanofibre diameter on the optical properties of the nanofibres are studied. The obtained results demonstrate that the diameter of the nanofibre increases; as expected, with increasing concentration of the PAN polymer in the electrospinning solution. In addition, the optical properties of the nanofibres depended on the type and concentration of the fluorescent agents. The fluorescence intensity increases with decreasing the fiber diameter only up to 0.008%wt fluorescent dye nanocomposite. In addition, the PL emission of the nanofibres containing the CQDs is found greater than that of the nanofibres containing the fluorescent dyes.

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